Acrylic Esters of Some Substituted Alkanols

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In an extensive study of copolymers of alkyl acrylates used in the development of the Lactoprene type of acrylic rubber,[2,3] need arose for acrylic esters containing additional functional groups to be used in the preparation of vulcanizable copolymers of ethyl or other alkyl acrylates.

The esters reported in this paper (Table I) include chloro-, bromo-, nitro-, cyano- and aralkyl acrylates, as well as two trichloroalkyl methacylates. The methacrylates were prepared by use of methacrylic anhydride.[4] 1,3-Dichloro-2-propyl acrylate was made from acrylyl chloride.[4] All the other acrylates were prepared by the alcoholysis of methyl or ethyl acrylate.[5] Efforts to prepare 2,2,2-trichloroethyl acrylate by the alcoholysis method resulted in no reaction. This is the only instance we have found in which a primary alkanol has failed to enter into the alcoholysis reaction with methyl or ethyl acrylate.

The esters in Table I were prepared for copolymerization with ethyl acrylate; hence their homopolymerization was not studied. Several of them were polymerized by heating with benzoyl peroxide in sealed tubes, and the brittle points[6] of the polymers were determined (Table I). Chlorine or bromine seems to raise the brittle points slightly, whereas the nitro group has a much stronger effect. The effect of the phenyl group appears to be intermediate between those of the halogens and the nitro group.

The polymers having brittle points above room temperature were hard and brittle at room temperature. The others were flexible and elastic. Those containing bromo or nitro groups were amber color; the others were substantially colorless. All were clear and transparent.

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Summary

Several bromo-, chloro-, nitro-, cyano- and aralkyl acrylates and two trichloroalkyl methacrylates were prepared.

Trichloroethanol, although a primary alcohol, did not alcoholyze ethyl acrylate.

The brittle points of alkyl polyacrylates were

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Mast, Rehberg, Dietz and Fisher, *Ind. Eng. Chem.*, **36**, 1022 1944).

(3) Mast and Fisher, *ibid.*, **40**, 107 (1948).

(4) Rehberg, Dixon and Fisher, This Journal, **67**, 208 (1945).

(5) Rehberg and Faucette, *J. Org. Chem.*, **14**, 1094 (1949).

(6) Rebberg and Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

TABLE I

PREPARATION AND PROPERTIES OF ACRYLIC ESTERS

Acrylate	Yield, %	Boiling point, °C.	Mm.	$n^{20}D$	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Cl, Br or N, % Calcd.	Cl, Br or N, % Found	Brittle pt. of polymer, °C.
2-Bromoethyl	74	53	5	1.4770	1.4774	34.24	34.24	33.6	33.5	3.9	4.0	44.6	44.2	−12[a]
3-Bromopropyl	70	96	18	1.4786	1.4106	38.86	38.78	37.3	37.1	4.7	4.6	41.4	41.1	
2,3-Dibromopropyl	94	105	6	1.5220	1.7803	46.63	46.60	26.5	26.2	3.0	2.9	58.7	57.9	
1-Bromo-2-propyl	80	69	10	1.4712	1.3885	38.86	38.86					41.4	41.2	
3-Chloropropyl	95	79	14	1.4522	1.1122	35.96	36.05					23.9	23.7	−14
2,3-Dichloropropyl	94	58	0.5	1.4765	1.2603	40.83	41.00					38.7	38.5	−10
1,3-Dichloro-2-propyl		50	1	1.4725	1.2592	40.83	40.76	39.4	38.9	4.4	4.5	38.7	38.6	5
2,2,2-Trichloroethyl[b]	56	55	1	1.4718	1.3264	45.70	45.90					48.8	48.4	90
2,2,2-Trichloro-*t*-butyl[b]	83	31	1	1.4657	1.2469	54.57	54.92	39.1	38.6	4.5	4.8	43.3	42.8	75[a]
2-Cyanoethyl	81	108	12	1.4409	1.0619	30.84	31.10	57.6	57.1	5.6	6.0	11.2	11.6	
2-Methyl-2-nitro-1-propyl[c]	94	95	5	1.4470	1.1162	41.33	41.45	48.5	48.3	6.4	6.6	8.1	7.9	32
2-Nitrobutyl[c]	73	63	1	1.4480	1.1172	41.33	41.49	48.5	48.0	6.4	6.8	8.1	7.7	
2-Phenylethyl	87	104	5	1.5111	1.0369	50.59	50.93	75.0	74.8	6.9	6.9			− 2

[a] Polymer appeared to be of low molecular weight. [b] Methacrylate. [c] These compounds were reported by Marans and Zelinski, THIS JOURNAL, 72, 2125 (1950), after the present work had been completed. The properties reported for the monomeric esters are in substantial agreement with ours. Our 2-methyl-2-nitro-1-propyl polyacrylate was hard and brittle at room temperature, whereas Marans and Zelinski reported theirs to be softer than methyl polyacrylate (which has a brittle point of about 0°).

raised slightly by halogen substituents, moderately by the phenyl group, and considerably by the nitro group.

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